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Newton leaves on potential energy surfaces

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Abstract. The reaction path (RP) is an important concept of theoretical chemistry. We generalize the definition of the Newton trajectory (NT), as an RP, to Newton leaves in a higher dimensional subspace of the configuration space. Our standpoint is that of Bofill and Anglada [(2001) *Theor. Chem. Acc.* 105:436], who used a “reduced potential energy surface” for finding an RP. An NT follows an RP curve where the gradient is always a pointer to a fixed direction. More generally, a Newton leaf is a subspace of coordinates where the gradient can move in a subspace of directions. We report some known mathematical properties of Newton leaves. We explain the construction of Newton leaves with the example of a 3D test surface in \mathbb{R}^4 [W.Quapp et al. (1998) *Theor. Chem. Acc.* 100:285], because three coordinate dimensions are the smallest number of dimensions one needs at least to understand a Newton leaf in contrast to the known NTs.

Keywords: Potential energy surface—Reaction path—Reaction subspace—Projection operator—Newton trajectory—Newton leaf

1 Introduction

The concept of the minimum energy path or reaction path (RP) of an adiabatic potential energy surface (PES) is the usual approach to the theoretical kinetics of larger chemical systems [1, 2]. It is roughly defined as a line in coordinate space which connects two minima by passing the saddle point (SP), the transition structure of a PES. The energy of the SP is assumed to be the highest value tracing along the RP. It is the minimal energy which a reaction needs to take place.

Reaction theories are based either implicitly (transition state theory), or explicitly (variational transition

state theory) on the knowledge of the RP [2]. These theories require local information about the PES along the RP only. They circumvent the dimension problem for medium-sized or large molecules: it is impossible to fully calculate their PES.

The location of an SP is an important question from a practical point of view, see Ref.[3] and references therein. The calculation of an RP is a proper tool to do that. The starting point is a 1D geometrically defined pathway which may serve as an RP. Geometrically defined means that only properties of the PES are taken into account, and that no dynamic behavior of the molecule is taken into consideration. In the driving-coordinate technique [4] one assumes that the reaction under consideration can be characterized by a coordinate, or a 1D direction being the linear combination of coordinates. The distinguished or driven coordinate method was developed to a more modern form as reduced gradient following (RGF) in Refs. [5,6], also called a Newton trajectory (NT) [7].

If one replaces the 1D search direction of an NT by a higher dimensional subspace of possible search directions, one works with the case of a reduced PES [3]. In mathematical terms it is the definition of a Newton leaf [8]. We repeat here the mathematical point of view of the reduced PES, and extend the 3D example of Ref. [9].

The note is organized as follows. Section 2 repeats some properties of PESs and special interesting points on PESs. Section 3 repeats the definition of reaction pathways, like NTs. In Sect. 4 their generalization to higher dimensions is given, the Newton leaves, and we execute a 3D example. In Sect. 5 we combine the Newton leaves and the definition of valley–ridge inflection (VRI) points. Section 6 is the conclusion.

2 Potential energy surface

The adiabatic PES of the molecular system of observation is the basis of our treatment. Using the Born–Oppenheimer approximation, we assume that the movements of the electrons and of the atom kernels are decoupled. The PES is the sum of the Coulomb -

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repulsion of the atom kernels and the Schrödinger equation of the electrons $\mathcal{H}\Psi = E\Psi$. The explicit calculation of the energy E is not of interest here. We assume the PES is given by a scalar function of the coordinates of the molecule at every point of interest:

Definition 1 Let \mathcal{K} be an open subset of \mathbb{R}^n . \mathcal{K} is the configuration space. Let $\mathbf{x} = (x_1, \dots, x_n) \in \mathcal{K}$. The function $E(\mathbf{x}) : \mathcal{K} \rightarrow \mathbb{R}$ is an n -dimensional (PES). The derivative $G : \mathcal{K} \rightarrow \mathbb{R}^n$ with

$$G(\mathbf{x})^T = \left(\frac{\partial E}{\partial x_1}(\mathbf{x}), \dots, \frac{\partial E}{\partial x_n}(\mathbf{x}) \right)$$

is the gradient, and the Hessian matrix $H(\mathbf{x}) \in \mathbb{R}^{n \times n}$ is

$$H(\mathbf{x}) = \left(\frac{\partial^2 E}{\partial x_i \partial x_j}(\mathbf{x}) \right)_{i,j=1}^n.$$

The configuration space of a molecule is restricted.

Definition 2 A point $\mathbf{x} \in \mathcal{K}$ is nondegenerate if $\det H(\mathbf{x}) \neq 0$. In the contrary case it is degenerate. The index of a nondegenerate point $\mathbf{x} \in \mathcal{K}$ is the number of negative eigenvalues of $H(\mathbf{x})$. We write $\text{ind}(\mathbf{x})$. A point $\mathbf{x}_0 \in \mathcal{K}$ with $G(\mathbf{x}_0) = \mathbf{0}$ is named a stationary point. A nondegenerate stationary point, \mathbf{x}_0 , is minimum if $\text{ind}(\mathbf{x}_0) = 0$, or maximum if $\text{ind}(\mathbf{x}_0) = n$, or saddle point of index i if $\text{ind}(\mathbf{x}_0) = i$, $0 < i < n$.

We assume that no stationary point is degenerate, i.e., that for all $\mathbf{x} \in \mathcal{K}$ the regularity condition holds:

$$\|G(\mathbf{x})\| + |\det H(\mathbf{x})| > 0. \quad (1)$$

Nondegenerate stationary points are isolated [10]. A special subset of degenerate points can be interpreted to be the branching points of RPs:

Definition 3 A VRI point is located where the gradient is orthogonal to a zero eigenvector of the Hessian [11].

VRIs are prerequisites of further treatments. At a VRI, the gradient does not lie in the kernel of the Hessian, and an augmented Hessian with a gradient does not lift the defect of the rank:

$$\begin{aligned} & \{\text{Set of all VRI points}\} \\ & = \{\mathbf{x} \in \mathcal{K} | \text{rank}[H(\mathbf{x}), G(\mathbf{x})] < n\}. \end{aligned} \quad (2)$$

The bracket means matrix augmentation: $[H(\mathbf{x}), G(\mathbf{x})] \in \mathbb{R}^{n \times (n+1)}$. Note that VRI points need not be symmetric [12]. VRI points are independent of any curve definition.

3 Newton trajectories

It is $S^{n-1} = \{\mathbf{x} \in \mathbb{R}^n | \|\mathbf{x}\| = 1\}$ the unit sphere in \mathbb{R}^n . We choose a column vector $\mathbf{r} \in S^{n-1}$ for a projection. We define a matrix $\mathcal{P}_r \in \mathbb{R}^{(n-1) \times n}$ by $(n-1)$ row vectors of \mathbb{R}^n being with r an orthonormal basis of \mathbb{R}^n . Thus $\ker(\mathcal{P}_r) = \text{lin}\{\mathbf{r}\}$ and $\text{im}(\mathcal{P}_r) = \text{lin}\{\mathbf{r}\}^\perp$. The construction of \mathcal{P}_r can be done by a Gram-Schmidt method [13]; or, if searching out a matrix in $\mathbb{R}^{n \times n}$, it can be done by the Householder transformation using the dyadic product of \mathbf{r} and \mathbf{r}^T [14].

The NT concept [3,5,6,15,16] is that a selected gradient direction is fixed along the curve $\mathbf{x}(t)$

$$G(\mathbf{x}(t)) / \|G(\mathbf{x}(t))\| = \mathbf{r}, \quad (3)$$

where \mathbf{r} is the unit vector of the search direction. The property in Eq. (3) is equivalent to a projection of the gradient. We pose

$$\mathcal{P}_r G(\mathbf{x}(t)) = \mathbf{0}. \quad (4)$$

\mathcal{P}_r is a constant $(n-1) \times n$ matrix of rank $n-1$. It projects in the direction of $\text{lin}\{\mathbf{r}\}$ and on $\text{lin}\{\mathbf{r}\}^\perp$.

Definition 4 The map $\mathcal{R} : \mathbb{R}^n \times S^{n-1} \rightarrow \mathbb{R}^{n-1}$, $\mathcal{R}(\mathbf{x}, \mathbf{r}) = \mathcal{P}_r G(\mathbf{x})$ will be called the reduced gradient, and $\mathbf{r} \in S^{n-1}$ will be called the search direction. Equation (4) is for any fixed $\mathbf{r} \in S^{n-1}$ the reduced gradient equation to the search direction \mathbf{r} .

The predictor-corrector method of the RGF [6] traces a curve Eq. (4) along its tangential vector. We use the derivative to obtain the tangent \mathbf{x}'

$$\mathbf{0} = \frac{d}{dt} [\mathcal{P}_r G(\mathbf{x}(t))] = \mathcal{P}_r \frac{dG(\mathbf{x}(t))}{dt} = \mathcal{P}_r H(\mathbf{x}(t)) \mathbf{x}'(t). \quad (5)$$

The RGF is a simple but effective procedure in order to determine all types of stationary points [5]. In the general good-natured case, each RGF curve passes each stationary point. A whole family of RGF curves connects the extrema if we vary the search direction \mathbf{r} [17], see Fig. 1. The test surface which may describe the H transfer in malonaldehyde [6] is used. It is

$$E(x, y) = 2y + y^2 + (y + 0.4x^2 + z^2)x^2. \quad (6)$$

There are two minima at around $(\pm 1.8, -2.7)$ and an SP at $(0, -1)$. It is easy to see that three VRIs are located on the PES: at $(0, 0)$, and at around $(\pm 1.8, -4.7)$. Their corresponding special NTs bifurcate [6].

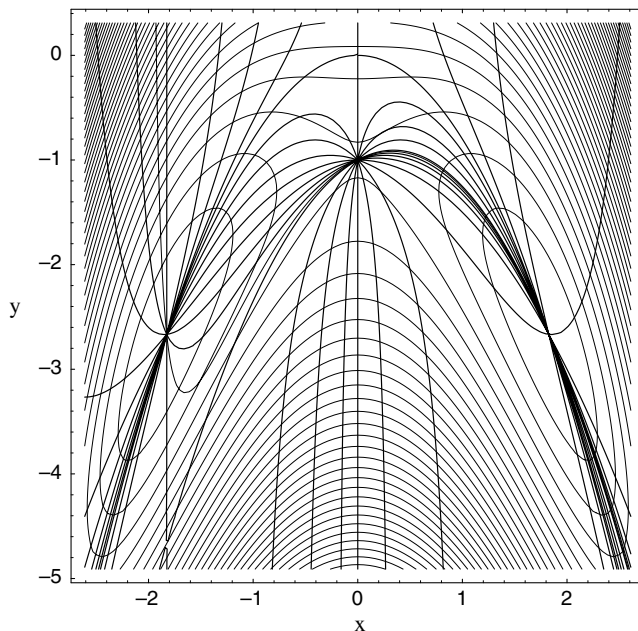


Fig. 1 A family of Newton trajectories(NTs) on a test Potential energy surface(PES) [6], Eq.(6)

Definition 5 Let $r \in S^{n-1}$. We will name the NT in \mathcal{H} to the direction \mathbf{r} as the set

$$\mathcal{T}_r := \{\mathbf{x} \in \mathcal{H} | G(\mathbf{x}) = r|G(\mathbf{x})|\}. \quad (7)$$

It is clear that \mathcal{T}_r is the set of solutions of Eq.(4). Or, in other words, it fulfills Eq.(3): the gradient points in the same direction [18]. For every nonstationary point the NT is given by the direction of the gradient [19].

4 Newton leaves and reduced PES

NTs can be generalized, if more than one search direction is possible. Diener [8, 20] has studied global aspects of the corresponding Newton leaves. Using again the gradient vector we define k -Newton leaves:

$$\mathcal{F}_V := \{\mathbf{x} \in \mathcal{H} | G(\mathbf{x}) \in V^\perp\}, \quad (8)$$

where V^\perp is a linear subspace of dimension k and the complement V is a linear subspace of dimension $n - k$. Of course, it is $V^\perp \cup V = \mathbb{R}^n$. An NT is a 1-Newton leaf in this definition, with $\dim V = n - 1$, and $V^\perp = \text{lin}\{r\}$ is the 1D subspace of the search direction. The n -leaf is \mathcal{H} itself. We will name V^\perp the **generalized search direction** of the k -Newton leaf \mathcal{F}_V . On a Newton leaf the gradient lies in the generalized search direction. A 0-Newton leaf ($V^\perp = \{\mathbf{0}\}$) is the set of all stationary points on \mathcal{H} . The rows of the projectors $\mathcal{P}_{V^\perp} : \mathbb{R}^n \rightarrow \mathbb{R}^{n-k}$ for the reduced gradient equation (in analogy to an equation like Eq. (4)) are formed by an orthonormal basis of V^\perp : $(n - k)$ vectors and are available by Gram-Schmidt orthogonalization [13]. The equation is again

$$\mathcal{P}_{V^\perp} G(\mathbf{x}) = 0. \quad (9)$$

The zero vector at the right hand side is $(n - k)$ dimensional.

Bofill, Anglada and coworkers generalized the RGF method to a reduced PES. They operated on Newton leaves without naming their objects in this way. The idea is that under a reaction only a part of the coordinates changes truly, and the remaining coordinates change only a little bit. The reduced PES is defined [3,15] by

$$V(\mathbf{x}_r) = \min_{\mathbf{x}_p} E(\mathbf{x}_p, \mathbf{x}_r), \quad (10)$$

where \mathbf{x}_r are coordinates of the reduced PES and \mathbf{x}_p are coordinates of directions with small changes. They will be adapted to an equilibrium [3]. The condition of the equilibrium is

$$(G_p)_i = \frac{\partial E(\mathbf{x}_p, \mathbf{x}_r)}{\partial \mathbf{x}_{p_i}} = 0, \quad i = 1, \dots, n - k, \quad (11)$$

where $(n - k)$ is the length of vector \mathbf{x}_p . In the frame of Newton leaves the reduced PES is a k -Newton leaf of the kind \mathcal{F}_V with $V = \text{lin}\{\mathbf{x}_p\}$. We will speak of a **PES reduced by V** . The generalized search direction of the PES reduced by V is the linear envelope of coordinates \mathbf{x}_r , i.e., V^\perp . With dimension of the reduced PES we mean the dimension of the generalized search direction V^\perp . Thus, Bofill, Anglada and coworkers applied Newton leaves [3,15]. It is important for this reason to cite some

properties of Newton leaves, i.e. of the reduced PESs, to aid our imagination. They are from the mathematical work of Diener [8, 20].

- If the dimension of the general search subspace becomes smaller, thus, if one cancels coordinates from the search, then the new reduced subspace is included in the former subspace. The new Newton leaf is in the former Newton leaf.

$$\text{If } V \subset W \text{ then } W^\perp \subset V^\perp, \text{ and then } \mathcal{F}_W \subset \mathcal{F}_V. \quad (12)$$

- Every reduced PES contains all stationary points of the PES. (Of course, it is this property which is employed by Bofill, Anglada and coworkers [3, 15].)

- In general, the reduced PES need not be connected. It can be composed of more components. (This is a possible drawback of the reduced PES. A clever choice of the search directions often circumvents the problem.)

- There is no component of a reduced PES (without the 0-leaf) which is only a stationary point.

- If \mathcal{F}_V is a k -leaf and $y \notin \mathcal{F}_V$ then there is an l -leaf \mathcal{F}_W with $l + k \leq n$ such that $y \in \mathcal{F}_W$ and

$$\mathcal{F}_V \cap \mathcal{F}_W = \{\text{set of all stationary points}\}.$$

- For the sum of two subspaces $(V + W)^\perp = V^\perp \cap W^\perp$ holds, and thus for two reduced PESs \mathcal{F}_V and \mathcal{F}_W

$$\mathcal{F}_{V+W} = \mathcal{F}_V \cap \mathcal{F}_W. \quad (13)$$

Since \mathcal{F}_V is a k -leaf, and \mathcal{F}_W is an l -leaf then $\mathcal{F}_U = \mathcal{F}_V \cap \mathcal{F}_W$ is an m -leaf with $k, l \geq m$ and $k + l - m \leq n$. In the example given later we will see that every NT in \mathbb{R}^3 is the intersection of two 2-Newton leaves in \mathbb{R}^3 .

- If the intersection of two reduced PESs with the generalized search directions V^\perp and W^\perp of dimension k and l contains further points besides the stationary points, then

$$n - k - l + 1 \leq \dim(W \cap V) \leq \min(n - k, n - l). \quad (14)$$

Especially, if an NT has a common nonstationary intersection point with a reduced PES, then the NT fully lies in the reduced PES.

- More generally, Newton leaves provide a ‘‘foliation’’ of \mathcal{H} . For all l with $1 \leq l \leq k$

$$\mathcal{F}_V = \bigcup_{W \supset V} \mathcal{F}_W \quad (15)$$

Thus, \mathcal{F}_V is the union of all l -leaves contained in there.

Example for reduced PES: We used the 3D model PES in Ref. [6]

$$E(x, y, z) = 2y + y^2 + (y + 0.4x^2 + z^2)x^2 + 0.01z^2 \quad (16)$$

to study the event of RP branching. The NTs were the tool for this study. The surface (Eq.16) can be seen for a model of proton transfer in malonaldehyde. It represents the H vibration in the O–H–O fragment. If d_1 is the O₁–H distance, and d_2 is the O₂–H distance, the coordinates used are $x = d_1 - d_2$ and y is motion along the O₁–O₂ stretch. The z -axis may indicate an out-of-plane vibration. The minima are at $(\pm\sqrt{10/3}, -8/3, 0)$ and the SP of index 1 is at $(0, -1, 0)$.

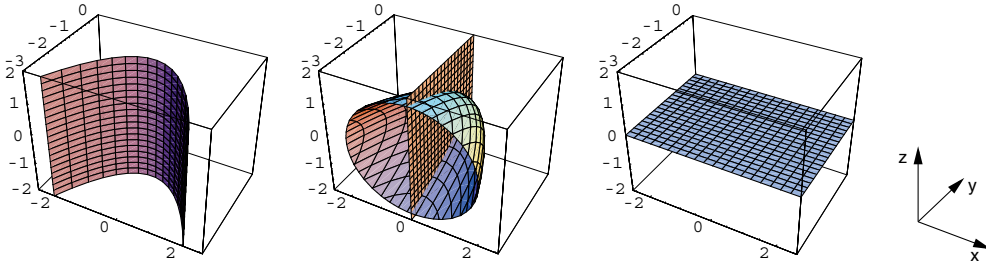


Fig 2 Three 2-leaves that are 2D PESs which are reduced by the coordinate axes V of the model surface (Eq.16) of ref[6]. From left to right V is $\text{lin}\{(0, 1, 0)^T\}$, $\text{lin}\{(1, 0, 0)^T\}$ and $\text{lin}\{(0, 0, 1)^T\}$

Figure 2 shows the three 2D PESs reduced by one coordinate direction, respectively, of the 3D PES (Eq.16). The surfaces are calculated by solution of the equation

$$G(\mathbf{x}) \cdot \mathbf{v} = 0, \quad (17)$$

where \mathbf{v} is the coordinate, by which the full 3D PES is reduced. The gradient is

$$G(x, y, z) = 2 \begin{pmatrix} x(0.8x^2 + y + z^2) \\ 1 + 0.5x^2 + y \\ (0.01 + x^2)z \end{pmatrix} \quad (18)$$

The reduced PES on the left in Fig. 2 is reduced by the y -axis, i.e. by $\mathbf{v}_2 = (0, 1, 0)^T$; Eq. (17) for the surface is $1 + 0.5x^2 + y = 0$. It is a 2-Newton leaf \mathcal{F}_V with $V = \text{lin}\{\mathbf{v}_2\}$; the subspace of the generalized search directions is $\text{lin}\{(1, 0, 0)^T, (0, 0, 1)^T\}$. The reduced PES on the right is \mathcal{F}_W , where $W = \text{lin}\{(0, 0, 1)^T\}$. The generalized search directions for \mathcal{F}_W are $\text{lin}\{(1, 0, 0)^T, (0, 1, 0)^T\}$. The intersection of \mathcal{F}_V and \mathcal{F}_W is the set of those points where the gradient stands orthogonally on V and on W , thus the 1-Newton leaf \mathcal{F}_{V+W} , with $V + W = \text{lin}\{(0, 1, 0)^T, (0, 0, 1)^T\}$. The search direction of \mathcal{F}_{V+W} becomes $\text{lin}\{(1, 0, 0)^T\}$. \mathcal{F}_{V+W} is the NT to the x -axis as the search direction, depicted on the right of Fig. 3 by a capital X.

The intersection of all three reduced PESs are the stationary points of the PES.

Fig 3 Common picture of all three 2D reduced PESs of Fig.2. The intersection of two 2-Newton leaves, respectively, is a NT, a 1-Newton leaf, see text and Fig. 6 in Ref. [6]. The intersection of all three 2D reduced PESs are the stationary points of the PES, the Saddle point and the two minima.

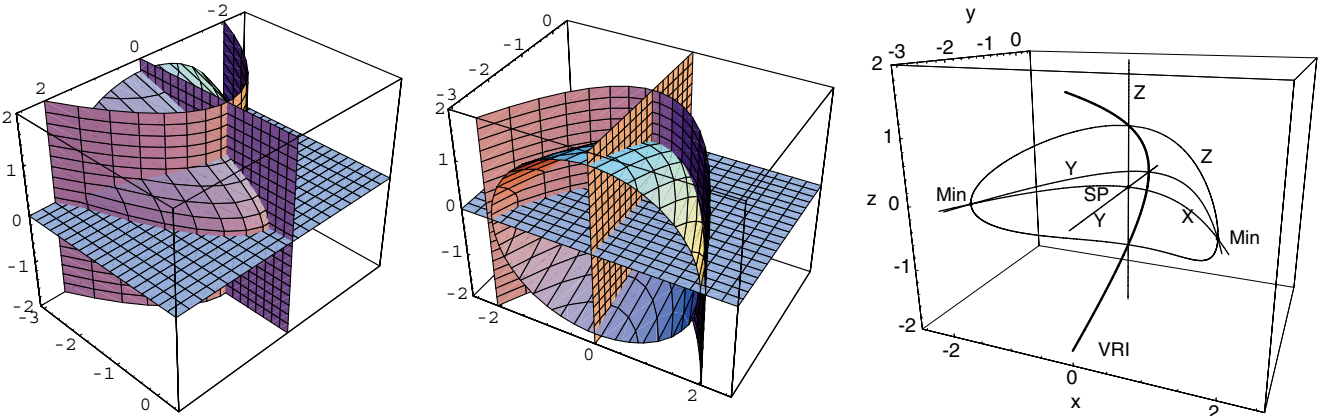


Figure 4 shows two 2-leaves with nonsymmetric search subspace.

5 Newton leaves and VRI points

The map $P_r H(\mathbf{x}) \rightarrow \mathbf{t}$ is smooth for the set of all $(n-1) \times n$ -matrices with maximal rank [21]. But there are singularities of definition 3 in points $\mathbf{x} \in \mathcal{H}$ where the rank of $P_r H(\mathbf{x})$ is smaller than $n-1$.

The Newton trajectory branches there. Thus, the VRI points are the branching points of 1-leaves.

We extend the VRI definition to Newton leaves. Let v_1, \dots, v_k be a basis of V^\perp , and let V^\perp include the gradient. Then a point $\mathbf{x} \in \mathcal{F}_V$ is a generalized VRI (gVRI) point iff

$$\text{rank} [H, v_1, \dots, v_k] < n. \quad (19)$$

Like in definition 3 the direction vectors v_1, \dots, v_k cannot raise the singularity of H in an augmented matrix if they are orthogonal to the zero eigenvector. One has [8,18,20]

– Let \mathbf{x} be a gVRI of a k -leaf \mathcal{F}_V . If a Newton leaf $\mathcal{F}_W \subset \mathcal{F}_V$ and $\mathbf{x} \in \mathcal{F}_W$ then \mathbf{x} is gVRI of \mathcal{F}_W .

– Let $k < \text{rank} H$ with k from the k -leaf \mathcal{F}_V . Then there is an l -leaf \mathcal{F}_W with $\mathcal{F}_W \supset \mathcal{F}_V$ such that the gVRI \mathbf{x} of \mathcal{F}_V is not a gVRI of \mathcal{F}_W . W can be chosen such that

$$l = k + \dim(\ker H) \cap V. \quad (20)$$

The gVRIs are special points for branchings as well as intersections. We will name two leaves \mathcal{F}_V and \mathcal{F}_W as oblique if neither $\mathcal{F}_V \subset \mathcal{F}_W$ nor $\mathcal{F}_W \subset \mathcal{F}_V$. If so, then the tangent spaces of \mathcal{F}_V and \mathcal{F}_W are oblique to each other in any point $\mathbf{x} \in \mathcal{F}_V \cap \mathcal{F}_W$ which is not a gVRI.

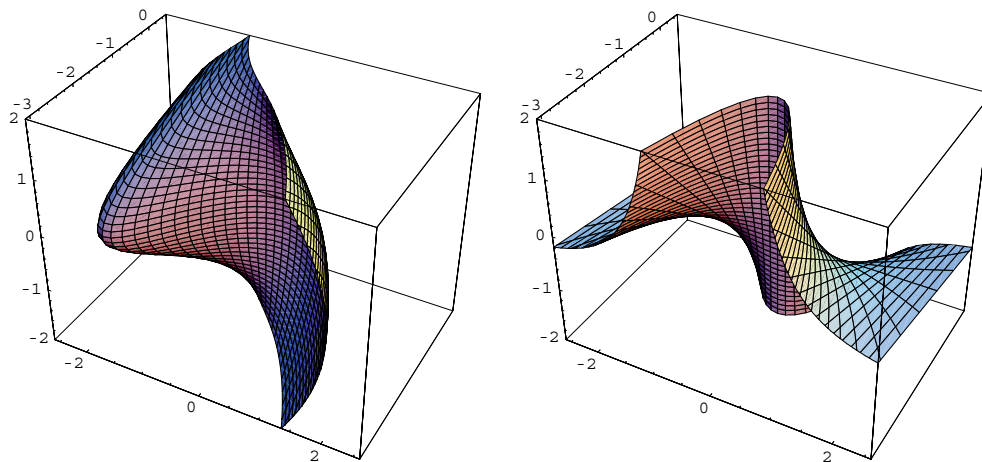


Fig. 4 2D PES reduced by V on the model surface (Eq.16). *Left:* $V = \text{lin}\{(0.35, 1, 0)^T\}$, *right:* $V = \text{lin}\{(0, 1, 1)^T\}$

The VRIs of the surface represented by Eq.(16) are on the parabola $y = -z^2$ in the (y, z) plane with $x = 0$, see Fig. 3, right. The gradient and Hessian are

$$G(0, -z^2, z) = 2 \begin{pmatrix} 0 \\ 1 - z^2 \\ 0.01z \end{pmatrix} \quad \text{and} \quad H = 2 \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0.01 \end{pmatrix} \quad (21)$$

The 2-leaf \mathcal{F}_V to $V = \mathbf{v}_2 = (0, 1, 0)^T$ crosses the VRI parabola at points $z = \pm 1, y = -1, x = 0$. The gradient, G , is in the linear combination of the basis vectors $\mathbf{v}_1 = (1, 0, 0)^T$ and $\mathbf{v}_3 = (0, 0, 1)^T$ of V^\perp . However, the augmented matrix $[H, \mathbf{v}_1, \mathbf{v}_3]$ has rank 3, thus, the points $(0, -1, \pm 1)$ are not gVRIs of the 2-leaf, but they are VRIs belonging to a 1-leaf, the NT Z in Fig. 3, right.

The central part of Fig. 2 is the 2-leaf to $V = \mathbf{v}_1 = (1, 0, 0)^T$. There are two solutions of Eq.(17): the plane $x = 0$, and the paraboloid $y = -0.8x^2 - z^2$. The VRI manifold $x = 0, y = -z^2$ lies totally inside this 2-leaf. The basis of V^\perp is $(\mathbf{v}_2, \mathbf{v}_3)$, and on the VRI parabola $\text{rank}[H, \mathbf{v}_2, \mathbf{v}_3] = 2 < 3$ holds throughout. Thus for this 2-leaf the VRI points of the NTs are also gVRIs of the 2-leaf.

6. Conclusion

The RP is a tool of theoretical chemistry without direct physical meaning [2]. The task of a geometrical treatment of the PES is to search pathways with a given property: to connect the minimum and the SP by a curve. The search of such pathways can also be done in higher dimensional subspaces; it need not be restricted to a 1D RP.

1D RPs can be defined by NTs, but higher dimensional searches can be defined by Newton leaves. We took up a proposal of Bofill and Anglada [3] in this note and reported the known mathematical properties of the Newton leaves [8]. In an example with the possibly lowest dimension of 3 we illustrated the interesting structure of Newton leaves.

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